

# PATENT SPECIFICATION

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## (54) FLAME PROOFING TEXTILES

(71) We, REICHHOLD-ALBERT-CHEMIE A.G., a German Body Corporate of Iverstrasse-57, Hamburg 70, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the production of flame-proof textiles with phosphorus. The term "flame-proof" is used herein to denote a substantially reduced level of combustibility compared with the untreated textiles.

It has been proposed to flame-proof hydrophobic synthetic fibres, optionally in admixture with natural fibres or with hydrophilic synthetic fibres, by treatment with halogen-containing phosphine oxides. It has also been proposed to impregnate cellulose-containing material with an aqueous solution of a tetrakis-(hydroxymethyl)-phosphonium salt and after drying the material to purify same with ammonia. However, a simpler process was desired in place of such a two-stage process.

It has further been proposed to make polyurethane foam materials flame-proof by adding red phosphorus. However, this is not in connection with the treatment of textiles. Treated textiles cannot be compared with such substances as synthetic resins are only present in limited quantities therein, most of the substances being formed by the readily combustible textile portion.

It has also been proposed to mix red phosphorus, optionally together with calcium borate, with substances having a hardenable synthetic resin base.

According to the present invention there is provided a process for the manufacture of textiles of improved flame-proof properties in which the textiles are treated with a synthetic resin and red phosphorus either in admixture or separately.

The phosphorus in free form as red phosphorus

is used in admixture with synthetic resins, preferably phenolic resins, optionally together with hardeners such as hexamethylenetetramine (with phenolic resins). In this form it can be used in the solid phase e.g. in finely particulate form with an average particle size of less than 100, preferably less than 40 microns. For example a mixture of novolac and red phosphorus and optionally hexamethylene tetramine can be prepared by grinding them together. The phosphorus mixed with the resin can e.g. be scattered or dusted onto the textiles in the form of flakes, grains or as a powder or be applied electrostatically. It is also, however, possible to apply the phosphorus and the synthetic resin to the textiles in a liquid medium e.g. as a dispersion such as a suspension of the phosphorus in the resin or in another distributing agent e.g. in an aqueous phase or in a melt e.g. of the resin, or as an emulsion. The phosphorus can thereby be dispersed in the resin or dissolved to form a true solution.

Although the phosphorus is conveniently applied in admixture with the synthetic resin, it may be applied separately either before or after treatment with the synthetic resin.

If the phosphorus is applied in a liquid medium it can be incorporated into the textiles by e.g. spraying, coating or dipping. The textiles can optionally be subsequently squeezed. Although when applying solid phosphorus from a suspension or melt of the resin no additional solvent or dispersing agent is present as a distributing agent, surprisingly products can be obtained with a very uniform distribution of the phosphorus over the entire surface of the textiles and over the entire cross-section of the textile layer.

The phosphorus is appropriately added in such a quantity that the textiles contain phosphorus in a quantity of 0.2 to 12 preferably 1 to 7 percent by weight calculated as  $P_2O_5$ . The phosphorus percentage can however vary according to the chemical structure of the syn-

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thetic resin used and the combustibility of the textiles. In the case of textiles with a high nitrogen content and textiles with a proportion of difficultly combustible fibre e.g. mineral fibres, generally a low phosphorus content is adequate.

Suitable synthetic resins for use with red phosphorus are e.g. phenolic resins, preferably solid, in the forms of resoles or novolacs, the latter being optionally mixed with hexamethylenetetramine or other hardeners; aminoplast resins e.g. melamine resins or urea resins; epoxy resins; polyesters; polyaddition resins e.g. polyolefins such as polyethylene, or vinyl resins such as polyvinyl acetate and vinyl acetate copolymers. Mixtures of resins may also be employed. When using condensation resins the synthetic resin mixture can also contain isocyanates.

The compositions comprising phosphorus can also be used in conjunction with the conventional additives such as accelerators; hardeners e.g. amines, acid anhydrides, Lewis acids and borofluoride compounds such as are conventionally used for epoxy resins; fillers such as silicic acid, silicates such as talc, or limestone; other flame-resistant additives such as boric acid or borates, e.g. calcium borate, or antimony oxide; and in the case of unsaturated polyesters also copolymerisable monomers such as vinyl and/or allyl compounds e.g. styrene, vinyl toluene, diallylphthalate may be present.

The textiles can be of different types e.g. natural fibres such as wool, cotton, hard fibres such as sisal or hemp, man-made fibres such as regenerated cellulose and its derivatives, e.g. rayon, polyamides, polyesters and optionally also mixtures of these fibres can all be used.

The textiles are preferably used in the form of a web, but they also may be used as a fleece. Cotton wool textile webs are loose laminar structures made from textile fibres or worked-up textile waste stuck together with relatively small quantities of synthetic resins. To prepare the flame-proof textiles e.g. finely ground synthetic resin particles are scattered onto the web before bonding. Subsequent heating causes a punctiform connection of the fibres by the synthetic resin.

However, the textiles to be treated can also be used as fabrics, plaited fabrics, warp knitted fabrics or knitted fabrics.

If desired, the resin deposited on or impregnated into the fibres may subsequently be condensed by heating at an elevated temperature to effect hardening or strengthening respectively of the fibres.

Products obtained by the process of the invention may be used either in one or in several layers to form an insulating material. In the production of insulating materials with a large layer thickness it is possible to treat each of the original thinner layers with a composition

containing the phosphorus and the synthetic resin and subsequently combine these layers e.g. by pressing them together at elevated temperatures so as to form a composite of larger layer thickness. In this way laminated bodies of this type can be produced without difficulty. The preponderantly solid pulverulent resins e.g. phenol formaldehyde resins can e.g. simply be scattered onto the previously formed web. In a pneumatic web-forming bonding apparatus wherein fibres entrained in an air-stream are deposited as a non-woven web on a conveyor a relatively uniform distribution of the synthetic resin powder with the textile fibre material is achieved and the final web formation brought about. The cotton wool textile web obtained in this manner passes, accompanied by appropriate compression, through a hardening zone wherein resin such as phenolic resin is crosslinked e.g. within 5 to 10 minutes at a temperature of 120 to 250° C. and the cotton wool textile web receives the desired dimensionally stable properties. Depending on the resin content, the cotton wool textile supply and the degree of compression, in this manner dimensionally stable webs of varying density and weight per unit area can be produced. A textile web finished according to the invention, on the application of a flame forms a strongly porous coke-like structure resulting in good heat irradiation and therefore considerable fire protection and a greatly reduced deflagration effect.

Textile webs of this type exhibit even under the severest testing by a strong Bunsen burner flame a surprisingly good flame resistance and substantially no tendency to re-glow as soon as the flame is withdrawn. Compared with materials finished with halogen-containing flame-proof additives they have the additional advantage that when a flame is applied substantially no poisonous and irritant gases are formed. They cannot be considered inflammable when fire-tested according to DIN 53906. In addition the textiles do not subsequently smoulder.

According to one embodiment of the invention the textiles may be treated with such an amount of the phosphorus and synthetic resin that the final product contains up to 40% by weight of material derived from the treatment, i.e. phosphorus, synthetic resin, and conventional additives, such as fillers, accelerators and hardeners if present.

The process according to the invention has very varied applications, mainly for the production of acoustic and thermal insulants e.g. for vehicles, in the building industry, as sound-absorbent insulation for movable or fixed machines, as thermal insulation for refrigerating devices and cold storage rooms, for chemical apparatus, pipe lines, or as the lining or cladding for all types of apparatus. It is also possible to produce according to the pro-



cess of the invention flame-proof furnishing material such as curtains, cushions, theatrical backdrops etc.

5 In order that the invention may be better understood the following examples are given by way of illustration only.

10 In these examples the dimensions of the cotton wool textiles specimens are 95×76 mm and the thickness is 10 to 20 mm. According to the weight per unit area of the cotton wool textile webs the flame was applied for 10 to 14 seconds.

#### Example 1.

15 100 parts by weight of a novolac prepared from 1 mol of phenol and 0.8 mol of a formaldehyde with the addition of maleic acid as the catalyst according to the conventional process having a melting point (capillary method) of 80 to 90° C and a viscosity at 20° C in a 20 50% ethanol solution of 210 cP is intensively ground with 10 parts by weight of hexamethylenetetramine and 44 parts by weight of red phosphorus under inert gas. The particle size of the red phosphorus is in the range of the phenol novolac resin whereof the particle size distribution is 75% less than 40 25 microns. The phosphorus-containing binder is applied in conventional manner by sprinkling onto a pure cotton web so that the binder proportion is 30% by weight based on the textile substrate. The treated web is placed in a circulating air drying cabinet for 5 minutes at 200° C whereby the phenol resin is cured. A light 30 yellow dimensionally stable cotton wool textile web with a thickness of 10 mm, a bulk density of 50 kg/m<sup>3</sup> and a weight per unit area of 500 g/m<sup>2</sup> is obtained. The content of phosphorus calculated as P<sub>2</sub>O<sub>5</sub> in the web is 3.01% by weight or 4% by weight, calculated 40 as phosphorus. After a flame is applied for 10 seconds in accordance with DIN 53906 the flame is extinguished immediately without any subsequent smouldering being observed. The weight loss is 1.5%.

45 There was also no subsequent smouldering effect when a flame was applied for 300 seconds. The weight loss then was 9.5%.

#### Comparative Tests

50 A) The novolac - hexamethylenetetramine adduct given in Example 1 without any admixture of phosphorus is applied to the web of Example 1 in the same proportion. Testing according to DIN 53906 with a flame application of 15 seconds is accompanied by a considerable spread of the flame; the material has an after-burning duration of 12 seconds and a subsequent smouldering time of 102 55 seconds. After this period the web is completely destroyed.

60 B) A mixture of 100 parts by weight of the hardenable phenolic resin indicated in Example 1 and 20 parts by weight of calcium borate is used in the same way as in Example 1 to bind the cotton wool textile web men-

tioned therein. The B<sub>2</sub>O<sub>3</sub> content of the web 65 is 5.55%. On testing according to DIN 53906 with a flame application period of 10 seconds there was an after-burning period of 0 seconds but the material smouldered until the web was 70 100% destroyed.

#### Example 2.

A resol is prepared from 1 mol of phenol and 1.1 mol of formaldehyde according to the usual process using concentrated ammonia solution as the catalyst and this has a melting point of 72° C (capillary method) and a viscosity at 20° C in a 50% solution of ethylene glycol monoethylether of 820 cP. Subsequently the resin is mixed with 20% by weight of calcium borate and 3% by weight of red phosphorus based on the resin in a ball mill under inert gas and in the same way as described in Example 1 scattered onto a cotton wool textile web consisting of a fibre mixture of cotton, wool and synthetic fibres until the resin content based on the textile material is 25% by weight. Accompanied by slight compression the material is cured for 15 minutes at 180° C. An approximately 20 mm thick web is obtained with a density of 56 kg/m<sup>3</sup> and a weight per unit area of 1120 g/m<sup>2</sup> which after testing according to DIN 53906 with a flame application period of 15 seconds had an after-burning time and smouldering time of 0 seconds. The weight loss was 3.2%. 75 80 85 90 95

#### Example 3.

A solid epoxy resin produced by condensation of diphenylolpropane and epichlorohydrin in the presence of caustic soda solution is mixed with 4% by weight of dicyanodiamide and with 7% by weight based on the total mixture of red phosphorus. The mixture is finally ground under an inert gas. In the manner described in the previous Examples it is applied to the cotton textile web and subjected to heat hardening for a few minutes at 180 to 200° C. 100 105

#### Example 4.

70 g of a polyester having a basis of 222 g (1.5 mol) of phthalic anhydride, 98 g (1 mol) of maleic anhydride and 280 g (2.65 mol) of diethyleneglycol are dissolved in 30 g of styrene. This solution is mixed with 2% by weight based on the total mixture of finely ground red phosphorus. The thus obtained mixture is mixed with 0.5 g of cobalt naphthenate, 1 g of a 50% benzoyl peroxide paste in dimethylphthalate, and applied by spraying to a cotton or synthetic fibre textile web. After hardening for a few minutes at 150° C as in Example 3 a web with good flame-resistant properties is obtained. 110 115 120

#### Irradiation Testing

The pronounced self-extinguishing effect and in particular the smouldering resistance of phosphorus-containing phenol formaldehyde 125



- resins of Examples 1 and 2 is further demonstrated by the tests on the Schütze radiation device. The test method differs from the above-described process according to DIN 53906 in that a relatively high temperature immediately acts on the complete surface of the object to be tested. The Schütze test was preformed on 96×96 mm samples, the samples being 140 mm from the radiation source. Thus with a radiation intensity of 1 cal/cm<sup>2</sup> sec a surface temperature of the irradiated object of 750° C ± 15% is obtained. The test results are given in the following table.

Example Number	Irradiation Period (sec)	Extinguishing of the flame at the end of irradiation	Subsequent Smouldering Time (sec)
<b>Invention</b>			
1. Hardenable phenol novolac with 4% red phosphorus	15	5	0
2. Phenol resol with 20% calcium borate and 3% red phosphorus	15	3	0
<b>Comparative tests</b>			
A Hardenable phenol novolac corresponding to Example 1 but without additive	3	60*	120*
B Hardenable phenol novolac with 20% calcium borate without phosphorus	15	3	300

\* The web is completely destroyed after 60 sec but the subsequent smouldering continues.

#### WHAT WE CLAIM IS:—

1. A process for the manufacture of textiles of improved flame-proof properties in which the textiles are treated with a synthetic resin and red phosphorus either in admixture or separately.
2. A process as claimed in claim 1 in which the synthetic resin is a condensation resin.
3. A process as claimed in claim 2 in which the synthetic resin is a phenolic condensation resin.
4. A process as claimed in any one of claims 1 to 3 in which the phosphorus is used in such an amount that the treated textiles contain 0.2 to 12% by weight of phosphorus calculated as P<sub>2</sub>O<sub>5</sub>.
5. A process as claimed in claim 4 in which the phosphorus is used in such an amount that the treated textiles contain 1—7% by weight of phosphorus calculated as P<sub>2</sub>O<sub>5</sub>.
6. A process as claimed in any one of claims 1 to 5 in which the textiles are treated with a solid phosphorus-containing composition.
7. A process as claimed in any one of claims 1 to 5 in which textile fibres are treated with a composition containing the phosphorus and the synthetic resin whereafter the resin deposited on or impregnated into the fibres is subsequently condensed by heating at an elevated temperature to effect hardening or strengthening respectively of said fibres.
8. A process as claimed in claim 7 in which said composition is a solid pulverulent composition which is dusted onto the textile fibres.
9. A process as claimed in claim 7 in which said composition is a liquid composition.
10. A process as claimed in claim 9 in which the textile fibres are treated with a solution, dispersion or emulsion of the composition containing the phosphorus and the synthetic resin.
11. A process as claimed in claim 9 or 10 in which said liquid composition is sprayed onto the textile fibres.
12. A process as claimed in claim 9 or 10 in which the treatment is carried out by dipping the textile fibres into said liquid composition.
13. A process as claimed in any one of claims 7 to 10 in which said composition is coated onto the textile fibres.
14. A process as claimed in any one of claims 1 to 13 in which the synthetic resin is a phenol-formaldehyde novolac in combination with hexamethylenetetramine.
15. A process as claimed in any one of



- claims 1 to 14 in which the synthetic resin is present in combination with phosphorus and hardener, each having an average particle size less than 100  $\mu$ .
- 5 16. A process as claimed in claim 15 in which the average particle size is less than 40  $\mu$ .
- 10 17. A process as claimed in claim 15 or 16 in which the synthetic resin is a novolac and the hardener is hexamethylenetetramine.
18. A process as claimed in any one of claims 1 to 17 in which the final product contains up to 40% by weight of material derived from said treatment.
- 15 19. A process as claimed in any one of claims 1 to 18 in which calcium borate is additionally present as a flame-proofing substance in the treating composition.
- 20 20. A process as claimed in any one of claims 1 to 19 in which a filler is additionally present in the treating composition.
21. A process as claimed in any one of the preceding claims wherein first sheet textile material is treated with a composition containing the phosphorus and the synthetic resin and then a plurality of sheets of the treated material thus obtained are combined to form a composite material of greater thickness.
- 25 22. A process as claimed in any one of claims 1—5 or 14—20 wherein phosphorus is applied separately to said textile either before or after treatment with said synthetic resin.
- 30 23. A process as claimed in any one of the preceding claims substantially as described herein with particular reference to the Examples.
24. Textile material of improved flame-proof properties comprising a textile the fibres of which are at least in part coated with red phosphorus and a synthetic resin. 40
25. A textile material as claimed in claim 24 wherein the base textile material is of natural origin.
26. A textile material as claimed in claim 25 wherein the base textile material is wool, cotton, sisal, hemp or a combination of any of these. 45
27. A textile material as claimed in claim 24 wherein the base textile material is of synthetic origin. 50
28. A textile material as claimed in claim 27 wherein the base textile material is a polyamide, polyester, rayon or a combination of any of these.
29. A textile material as claimed in any one of claims 24 to 28 wherein the base textile material is a combination of material of natural and synthetic origin. 55
30. A textile material as claimed in any one of claims 24 to 29 in which the base textile material is in the form of a fleece. 60
31. A textile material of improved flame-proof properties whenever obtained by the process claimed in any one of claims 1 to 23.
32. Insulating material comprising a product as claimed in any one of claims 24 to 31. 65

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